

Structure of 3-bromo-4-methyl-7-ethoxycoumarin

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Abstract The title compound 3-bromo-4-methyl-7-ethoxycoumarin [$C_{12}H_{11}O_3Br$] having Br-atom at C3 belongs to the family of benzopyrones. The crystal structure has been determined at room temperature. Needle like crystals are monoclinic, space group $P2_1/n$ with unit cell dimensions $a = 7.890(3)$ Å, $b = 12.573(4)$ Å, $c = 11.390(7)$ Å, $\beta = 98.64(3)^\circ$ and $Z = 4$. The structure was solved by direct method and refined by full matrix least-squares method to a final $R = 0.048$ for 1573 observed reflections. The coumarin moiety is planar with the mean plane of the benzene ring making a dihedral angle of $2.0(3)^\circ$ with the pyrone ring. The Bromine atom lies in the plane of the coumarin moiety. The carbethoxy group at C7 makes a dihedral angle of $7.8(4)^\circ$ with the mean plane of the coumarin ring.

Keywords Coumarin, X-ray crystallography

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Coumarins with various substituents at position 3 exhibit variety of biological properties [1] and are of spectroscopic interest [2]. 3-bromo-4-hydroxy-coumarin exhibits antivitamin-K property and is shown to be a monohydrate [3]. Various substituents at C4 play a vital role in the structure activity relationship studies of the induction of drug metabolising enzymes by coumarin [4] and its wide tunability in the field of dye laser [5] is interesting. Crystal structure studies of 3-bromo-khellactone-methylether [6] and dibromoeristic [7] were useful in establishing the configuration of the respective natural products. During an attempted bromination of 4-methyl-7-ethoxycoumarin, the substitution occurred at position-3 and not at the C4 methyl group giving rise to 3-bromo-4-methyl-7-ethoxycoumarin. The position of bromine was established by the PMR spectrum which showed the absence of C3 proton around 6.5 ppm. In continuation of our crystal structure studies on 3-bromoacetylcoumarin [8]

and 3-acetyl-6-bromocoumarin [9], it was thought of interest to study the crystal structure of the title compound.

The title compound was synthesised by refluxing 4-methyl-7-ethoxy-coumarin (5g, 0.02ml) with N-bromo succinimide (NBS) (4.3g, 0.02ml) in 50ml of dry carbon-tetrachloride in the presence of catalytic quantity of dibenzoylperoxide for 5 hours. The reaction mixture was filtered and the filtrate was concentrated to obtain a colourless solid which was recrystallised from ethanol.

Intensity data were measured on Enraf-Nonius CAD4 diffractometer fitted with graphite-monochromatised MoK_α radiation, $\lambda = 0.7107$ Å. The crystallographic data has been tabulated in Table 1. The structure was solved by direct method and refined by full-matrix least-squares procedure based on F. Non-H atoms were refined with anisotropic thermal parameters. All hydrogen atoms have been geometrically fixed. All the scattering factors were as incorporated in NRCVAX [10] and SHELXL-97 [11] programs. The final positional and isotropic

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Table 1. Crystal data for the title compound

Crystal morphology	White
Crystal size	0.90 × 0.15 × 0.1
Chemical formula	C ₁₂ H ₁₁ O ₃ Br
Molecular weight	283.12
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Cell constants	<i>a</i> = 7.890(3) Å <i>b</i> = 12.573(4) Å <i>c</i> = 11.390(7) Å <i>β</i> = 98.64(3)°
Volume	1117.1(8) Å ³
Number of formula units <i>Z</i>	4
Density (calculated) <i>D_c</i>	1.695 g/cm ³
Absorption coefficient <i>μ</i> (MoK _α)	3.67 mm ⁻¹
Unique data measured	2597
Observed data with <i>I</i> ≥ 2.5σ (<i>I</i>)	1573
<i>R</i>	0.048
<i>R_w</i>	0.090
Maximum electron density	0.60 e/Å ³
Minimum electron density	-0.33 e/Å ³

thermal parameters of the non-hydrogen atoms are listed in Table 2. Figure 1 shows the chemical diagram of the molecule. ORTEP [12] of the molecule with thermal ellipsoids viewed along *b*-axis is shown in Figure 2. The selected bond lengths, angles and torsion angles are tabulated in Table 3.

Table 2. The final positional and equivalent isotropic thermal parameters (Å²) of the non-hydrogen atoms with e.s.d's in parentheses

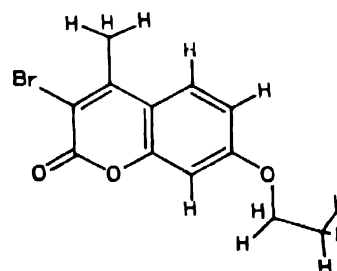
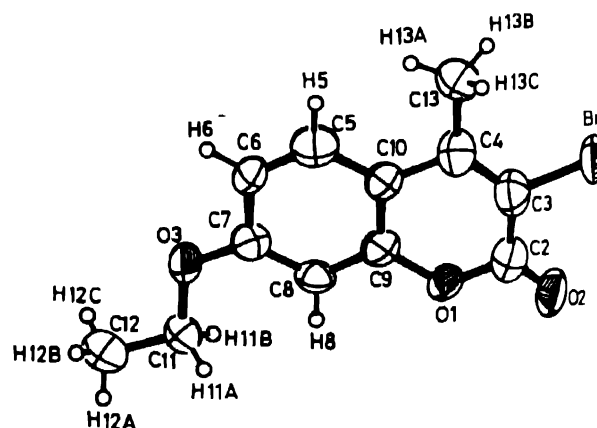
Atom	Ueq			
Br	0.3861(1)	0.1596(6)	0.1503(7)	0.0758(4)
O1	0.6997(7)	0.1557(3)	0.4695(4)	0.0638(1)
O2	0.5790(9)	0.2829(4)	0.3572(5)	0.0913(2)
O3	0.9984(6)	-0.1054(4)	0.7226(4)	0.0633(1)
C2	0.6001(9)	0.1891(6)	0.3681(7)	0.0685(2)
C3	0.5280(8)	0.1068(5)	0.2866(6)	0.0604(2)
C4	0.5604(8)	0.0014(6)	0.3041(5)	0.0577(1)
C5	0.7210(9)	0.1319(5)	0.4427(6)	0.0622(2)
C6	0.8265(1)	0.1558(5)	0.5443(6)	0.0631(2)
C7	0.8917(8)	-0.0747(5)	0.6243(5)	0.0567(1)
C8	0.8463(8)	0.0281(5)	0.5971(5)	0.0554(1)
C9	0.7382(8)	0.0496(4)	0.4919(5)	0.0541(1)
C10	0.6723(8)	-0.0289(4)	0.4114(5)	0.0537(1)
C11	1.0467(8)	-0.0253(6)	0.8100(5)	0.0594(2)
C12	1.1443(1)	-0.0779(7)	0.9178(6)	0.0755(2)
C13	0.4887(1)	-0.0834(6)	0.2198(6)	0.0717(2)

The coumarin moiety is about planar with C13, Br and O2 atoms lying in the least squares plane through C2–C10, O1 atoms. The ethoxy group at C7 makes a dihedral angle of 7.8(4)° with

Table 3. The selected bond lengths (Å), angles (°) and torsion angles of the molecule

Bond lengths			Bond lengths		
	Length		Length	Length	
Br–C3	1.893(6)	O1–C2	1.362(9)	O1–C9	1.383(7)
O3–C7	1.352(8)	O3–C11	1.427(8)	C2–O2	1.195(10)
C11–C12	1.501(10)	C13–C4	1.488(9)		
Bond Angles			Bond Angles		
	Angle		Angle	Angle	
C2–O1–C9	122.4(5)	C7–O3–C11	116.4(5)		
–	–	O2–C2–O1	116.5(7)	O2–C2–C3	127.1(7)
O1–C2–C3	116.4(6)	–	–	–	–
O3–C11–C12	108.0(6)	–	–	O1–C9–C10	120.8(5)
Torsion angles			Torsion angles		
	Torsion angle		Torsion angle	Torsion angle	
C11–O3–C7–C8	8.8(9)	–			
–	–	C9–O1–C2–C3	3.2(4)		
O1–C2–C3–C4	-2.9(1)	O2–C2–C3–Br	0.1(1)		
C2–O1–C9–C10	-1.5(1)	–			
		C4–C10–C9–O1	0.9(9)		
		Br–C3–C4–C13	0.3(1)		

the coumarin mean plane. The dihedral angle between the benzene and pyrone ring is 2.0(3)°.

**Figure 1.** Chemical diagram of the molecule**Figure 2.** ORTEP plot of the molecule with thermal ellipsoids viewed along *b*-axis.

The bonds C2-O2 1.195(1) Å and C3-C4 1.358(5) Å of the pyrone ring show distinctly double bond character [13]. The bonds C2-C3 1.448(7) Å and C4-C10 1.447(4) Å adjacent to the double bond are systematically longer than 1.40 Å [13,14]. It is interesting to note the increased bond length of C3-Br 1.893(6) Å and the shortening of C2-O2 1.195(1) Å which facilitates the minimization of dipole-dipole repulsion. Also O2-C2-O1 116.5(7)°, smaller than O2-C2-C3 127.1(7)° which may result from the steric effect of the substituent at C2 and C3.

The bond angles around C2 are 116.5(7)°, 116.4(6)° and 127.1(7)° which compare with 119.9(7)°, 112.8(7)° and 127.4(7)° respectively of coumarin [9] and resemble the geometry of a carboxylic group.

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